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(54) NEW POLYMER COMPOSITIONS AND THEIR PREPARATION

(71) We, UNIBRA, a Belgian Company of 40, Avenue des Arts, B 1040 Brussels, Belgium, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The invention relates to new polymer compositions containing polyester polymers, to their preparation and to the shaped articles obtained therefrom. More specifically, the polymer compositions of the invention are prepared from polycarbonate polymers and polyester polymers, wherein a polycarbonate polymer means a polymer the formula of which is that of a polyester formed between carbonic acid and an aromatic diol, preferably a bisphenol, whereas a polyester polymer has a formula deriving from an aliphatic or cyclo-aliphatic diol and an aromatic diacid, preferably a benzene-dicarboxylic compound.

The combination of aromatic polycarbonates with aromatic polyesters such as polyesters from terephthalic or isophthalic acid in one polymeric composition raises a problem of stability. Although the main two components of the composition are inherently stable and can be readily mixed together when in the molten state, mixing them however induces a reaction leading to a very fast degradation of the polymers and resulting in the formation of bubbles and foam, thus substantially prohibiting any commercial application. It should be noted that such drawbacks as the release of foam and bubbling are not encountered when mixing two polyester polymers together, such as polyethylene-terephthalate and polybutylene-terephthalate, without the polycarbonate polymer.

The invention relates to a process whereby the degradation reaction can be interrupted at any time by adding to the mixture comprising the polycarbonate and the polyester a stabilising additive.

Stable polycarbonate-polyester compositions may thus be produced, which show unexpected outstanding properties and can be moulded into shaped articles by any known moulding or other shaping technics.

In particular, the invention permits the production of a whole new range of polyester compositions, or so-called alloys, which lead, after suitable shaping, to articles having mechanical, physical and chemical properties which did not exist with other known polymers. In particular, the present invention makes it possible, through the formation of an alloy with a fairly heat-resistant amorphous polycarbonate (such as the conventional bisphenol polycarbonates), to improve the impact resistance and thermal resistance of crystalline polyesters such as polybutylene-terephthalate. It further allows the shape transformations at high temperature which are to be performed in particular when using extrusion or injection moulding technics and has the further advantage to lower the cost of the products, while retaining a high mechanical resistance at ordinary temperatures and a high resistance to organic solvents. In addition, the composition can be readily prepared and easily worked up. It can be obtained by simply mixing the components together.

A further advantage of the invention is that it makes it possible to produce compositions comprising a controlled proportion of polycarbonate-polyester copolymer, which constitute a completely new range of products showing specific properties which could not be expected from those of the individual polymer components.

According to the invention there is provided a process for preparing polyester polycarbonate compositions, as hereinbefore defined, comprising mixing at least one aromatic polyester polymer and at least one aromatic polycarbonate polymer in a reacting step wherein the polyester and the polycarbonate are contacted together in the molten state, at a temperature between 150°C and 300°C, for a time interval between 0.1 minute and 4 hours, then preventing the reaction between the polymers by adding to the melted mixture from 0.1% to 5% by weight with respect to the total polymer weight, of a stabilizing additive selected from phosphorus compounds and carboxylic acids.

A first class of additives which may be used in the process of the invention comprises the phosphorus containing derivatives, such as preferably the organic phosphites, it being understood that this term designates all the esters of phosphorous acid including those likely to appear under other forms. Thus, for instance, the phosphites used according to the invention include the diphosphites, which are likely to convert into phosphonates and are nevertheless usually called phosphites. But other phosphorous compounds can also be used, such as metaphosphoric acid, arylphosphinic and arylphosphonic acids. Preferred additives for carrying out the invention are those in which the phosphorous atom carries at least one and preferably two aromatic substituents such as the phenyl radical, on one hand, and diphosphites, and in particular those in which the carbon atom carries two alkyl radicals comprising from 4 to 30 carbon atoms, on the other hand. Other suitable additives may be selected from all organic phosphites having the following formula: $RP(OR)_2$, wherein each R may be a hydrogen atom, an alkyl radical having from 1 to 20 carbon atoms, or an aryl radical having from 6 to 20 carbon atoms, and wherein at least one of said R radicals is such an alkyl or aryl radical.

Generally, the use of phosphites as the additives shows various advantages, in particular that of being in the form of liquids or of solids having a low melting point, which renders their incorporation with the polymer mixture easier. Moreover, the large number of compounds belonging to the class of phosphites, permits to select the additive so as to provide the composition with additional desirable properties, e.g. fire resistance. Of course, mixtures of such additives may be used in the compositions of the invention.

Another class of suitable additives is comprised of the carboxylic acids, i.e. organic compounds the molecule of which comprises at least one carboxy group.

Preferred acids are the organic compounds of the aromatic series comprising at least two, or preferably three or four, carboxy groups as substituents on a benzene ring.

The acids may be derived from the corresponding anhydrides. Thus, anhydrides may also constitute the additives of the invention, preferably provided that water is present in sufficient amounts to ensure at least partial hydrolysis of the anhydrides.

Specific additives from this class may be non aromatic acids such as stearic acid, or preferably aromatic acids such as terephthalic, trimellitic, trimesic, pyromellitic acids. They may further be anhydrides such as the anhydride of tetrahydrofurane-tetracarboxylic acid or the anhydrides of aromatic acids comprising at least three carboxy groups, such as trimellitic, pyromellitic, and naphthalene-tetracarboxylic acids, such anhydrides being preferably partially hydrolyzed.

The present invention applies to all compositions wherein the polymers are essentially constituted, partly by one or more aromatic polycarbonates, in particular a bisphenol-polycarbonate, and preferably a polycarbonate of a 4,4'-dihydroxy diphenyl alkane, a typical example being polycarbonate of bisphenol A (polycarbonate of 4,4'-dihydroxy 2,2-diphenyl propane) and, partly, by an aromatic polyester, in particular a polyester derived from an aliphatic glycol, preferably a straight-chained aliphatic glycol, or a cycloaliphatic glycol, which comprises from 2 to 10 carbon atoms, and from a benzene dicarboxylic acid, preferably terephthalic acid, isophthalic acid or their mixtures.

In preferred compositions of the invention, the polyester is, more specifically, polybutylene terephthalate; however, this is by no means restrictive, since additives of the phosphite or carboxylic acid types have proved efficient with other similar

polyesters admixed with polycarbonates. A mixture of different aromatic polyesters can also be used, preferred mixtures of this kind being those containing both polyethylene-terephthalate and polybutylene-terephthalate.

In the compositions according to the invention, the two polymers can be present in any proportions, preferred compositions comprising from 5 to 95 parts, and preferably from 20 to 80 parts of the polycarbonate, by weight, and respectively from 95 to 5 parts, and preferably from 80 to 20 parts of the polyester. Moreover, polycarbonates with a molecular weight higher than, or at least equal to 30,000 (by weight) and polyesters (in particular, polybutylene terephthalate) with a molecular-weight higher than, or at least equal to 30,000 (by number) have proved preferable in order to obtain polymer alloys which may be formed into moulded articles which show improved impact resistance and thermal resistance with respect to conventional crystalline polybutylene terephthalate.

The percentage of additives introduced into the composition according to the invention is, preferably, from 0.25% to 1% by weight, with respect to the total polymer weight; however, other percentages, usually between 0.1% and 5% by weight, can be resorted to.

In carrying out the process of the invention, mixing of the components may be performed at any temperature above the melting temperature of the individual polymers and preferably between 150 and 300°C.

In a preferred embodiment of the invention, the polymers are allowed to react together in the molten state, for a time interval of from 1 minute to 4 hours, and preferably from 1 minute to 100 minutes, before the stabilizing additive is incorporated into the mixture. Copolyesters are thus obtained wherein the chemical reaction prior to stabilization by the additive provides the grafting of polyester blocks, the length of which varies according to the extent of the reaction having taken place, onto polycarbonate chains.

In preferred compositions of the invention, from 0.1 to 80% of the number of carboxy groups from the polyester are engaged in ester linkages with aromatic rings. That means that a proportion of the polyester and polycarbonate have reacted with one another and formed a copolyester. In the copolyester, linkages are formed between carboxy groups from the polyester and aromatic rings from the polycarbonate, whereas the carboxy groups are esterified with aliphatic or cycloaliphatic moieties from the diol in the original polyester. The ratio of the number of carboxy groups esterified with aromatic groups with respect to the total number of carboxy groups (esterified or not, with aromatic aliphatic or cycloaliphatic groups) is used as an indication of the "copolyesterification rate" or copolymer proportion.

In particularly valuable compositions of the invention, the copolyesterification rate in the copolyester compositions of the invention is less than 10%, preferably from 1% to 6%, and more preferably from 2.5% to 5%. It is quite surprising that transparent insoluble moulded products can be thus obtained. In such case, the polymers in the composition preferably comprise from 40 to 80% by weight polycarbonate and from 60 to 20% by weight polyester.

The above copolyesterification rate can be obtained for instance by the method comprising the steps of, first mixing the polycarbonate and the polyester in the molten state, allowing them to react at a high temperature, generally within the range from the melting temperature of the polyester to 300°C, and in the specific case wherein the polyester is polybutylene terephthalate, at a temperature preferably of about 250°C, for a time interval which can be of from about 1 to 30 minutes, and preferably from 2.5 to 20 minutes, then incorporating the additive.

According to another specific embodiment, the composition also contains a strengthening filler, which may comprise inorganic or organic fibres or other particles (in particular, glass fibres), in proportions from about 5 to 40% of the composition overall weight, and, preferably, from 10 to 20% by weight.

It is known that glass fibres increase the mechanical properties, and specially the impact resistance of polyesters such as polybutylene-terephthalate. However, a similar increase can be obtained, without glass fibres, in compositions of the invention containing for instance half polybutylene terephthalate and half polycarbonate. Although the addition of glass fibres in such compositions further increases the impact resistance, the invention thus makes it possible to reduce the amount of glass fibres.

In all cases, the compositions of the invention can be easily prepared. The components may be mixed together, and contingently together with other conventional components, by the usual technics of the industry of polymers.

Mixing can be carried out or completed while the composition is being worked

up, in particular in the course of a shaping operation carried out under heat and pressure.

The outstanding thermal stability of the thus formed polymer compositions permits to carry out all sorts of transformations, including extrusion and injection, from commercial polymers, without any lengthy and costly chemical conversion.

The invention will be more clearly understood from specific examples which however should by no means restrict the scope of the invention. In the following examples, percentages are given by weight (unless otherwise stated) and the word "alloy" refers to a composition wherein the additive is incorporated early after the beginning of the mixing steps, (i.e., less than 1 minute), whereas the word "copolyester" designates a composition wherein the incorporation of the additive is postponed (more than 1 minute) so as to allow a substantial controlled chemical reaction between the two polymers. Moreover, abbreviated forms "PC", "PBT", "PET", and "PCHDT", will be used hereafter, from time to time, for designating bis-phenol A polycarbonate, polybutylene-terephthalate, polyethylene-terephthalate, and poly(cyclohexylene-dimethylene) terephthalate/isophthalate, respectively.

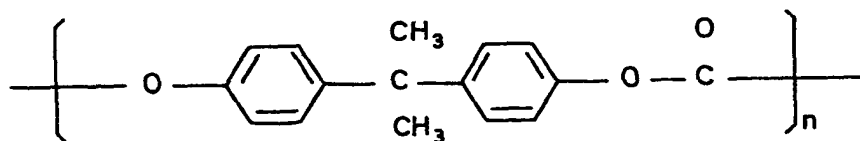
Within the scope of the invention, mixtures of such polyesters are used in some examples or copolymers of such polyesters, for instance a copolymer of PBT and polytetramethylene-glycol.

Example I.

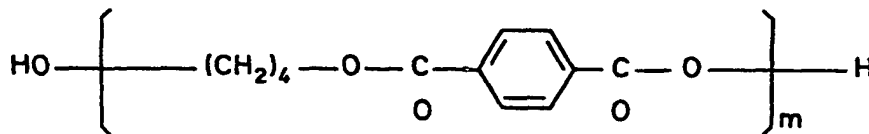
In a reference experiment, 50% by weight of bis-phenol A-polycarbonate (trade-mark "LEXAN 135" of General Electric) are mixed with 50% of polybutylene-terephthalate (trade-mark "TENITE 6PRO" of Eastman Kodak) in a roller-mixer at the temperature of 250°C. Then the thus obtained mixture is moulded under pressure at the temperature of 270°C. A non homogeneous brown mixture is obtained wherein gas bubbles indicate a noticeable degradation. The full cycle, in that instance, lasts 10 minutes. If the time is longer or the temperature higher, foam is formed and prohibits any transformation. Under such circumstances, quite obviously the mixture can by no means be worked up in an injection-press, which would require temperatures of about 270°C for polycarbonate-terephthalate. The alloy instability which in the present instance is revealed by a release of gas, is encountered as well with all other PC—PBT mixtures, whatever be the components selected from commercially available polymers.

In another experiment, alloys according to the invention are prepared by mixing 50% by weight of bis-phenol A-polycarbonate and 50% of polybutylene-terephthalate with 0.5% by weight of various additives, to be specified hereafter, all of which are phosphorus containing compounds. The polymers used are the same as above.

Bis-phenol A-polycarbonate has the following formula:



whereas polybutylene-terephthalate has the formula:



wherein n and m are integers which vary according to the polymer molecular weight.

In this particular example, the molecular weight by weight of the polycarbonate was of about 45,000 and the molecular weight, by number, of the polycarbonate-terephthalate was of about 41,000. In this example as well as in the full wing ones, the weight molecular weight (\overline{M}_w) of the polycarbonate is determined by viscosity measurements in dioxane at 30°C, using the following formula:

$$(\eta) = 4.76 \times 10^{-4} (\overline{M}_w)^{0.68}$$

and the number molecular weight (\overline{M}_n) of polybutylene-terephthalate is determined by viscosity measurements in a 60/40 phenol/tetrachlorethane mixture at 25°C, using the following formula:

$$(\eta) = 1.93 \times 10^{-4} (\overline{M}_n)^{0.82}$$

In the present example, mixing the two polymers together with the additive is carried out at the temperature of 260°C, in a roller-mixer, for 5 minutes. Then, a sample is pressed for 5 further minutes, at 240°C. Finally, at the temperature of 260°C, by means of a capillary rheometer, the thermal stability of the mixture (determined by the time expired until a gas release occurs within the extrudate) is measured. The extrudate is examined every fifth minute up to 140 minutes from the beginning of the test. That stability time, which is in fact a measurement of the efficiency of the additives used, is mentioned hereinafter for various phosphorus containing compounds.

		<u>Stability time (mn)</u>
	No additive	below 5
	Di-n-octadecyl phosphite	above 140
	Tri-phenyl phosphite	above 140
	Di-phenyl phosphite	70
	Di-benzyl phosphite	50
	Decyl-diphenyl phosphite	50
	Phenyl didecyl phosphite	30
	Metaphosphoric acid	20
	Phenyl phosphoric acid	65
	Phenyl phosphinic acid	50

When visually inspected, the samples appeared as white and opaque, with no trace of gas release. The additives of the diphosphite type (and, more especially, di-n-octadecyl phosphite) ensure an absence of colouration more thoroughly than triphosphites. They provide samples with a perfect appearance and an outstanding surface condition, which do not stick to the mould.

Moreover, it appears from the above table that the efficiency of triphosphites with respect to stabilization is all the more pronounced as they comprise more aromatic substituents on the phosphorus atom.

Example II.

According to the invention, following the same operating steps as in Example I, alloys are examined, containing 0.5% by weight of di-n-octadecyl phosphite as an additive, said alloys differing from one another in that polymers of various origins are used, which implicates various molecular weights. The stability times measured are given in the following table, in which the bis-phenol A-polycarbonate (PC) is

characterized by its molecular weight by weight (\overline{M}_w), whereas the polybutylene-terephthalate (PBT) is characterized by its molecular weight in number (\overline{M}_n).

5	PC (50% by weight) (\overline{M}_w)	PBT (50% by weight) (\overline{M}_w)	Stability time (minutes)	5
	45,000	38,000	120	
	45,000	27,000	50	
	45,000	29,000	55	
	45,000	38,000	120	
10	45,000	41,000	above 140	10
	30,000	41,000	30	

Example III

Following the same procedure as in Example I, samples are prepared from bis-phenol A-polycarbonate and polybutylene-terephthalate, stabilized by means of an organic phosphite constituted by di-n-octadecyl phosphite, used in the amount of 0.5% by weight.

The stability times, measured at the temperature of 260°C, are given hereinafter with respect to the percentages of the polymers.

20	PC (% by weight)	PBT (% by weight)	Stability time (minutes)	20
	80	20	above 140	
	60	40	above 140	
	50	50	above 140	
	40	60	above 140	
25	20	80	above 140	25

Thus, independently of the relative percentages of the basic two polymers, the stabilization of the alloys is ensured for more than 140 minutes, viz. the limit of the measurement as carried out.

Example IV.

With the same operating steps as in Example I, while varying the amount of additive from one sample to another, the following results are obtained:

30	Additive	Concentration (% by weight)	Stability time (minutes)	30
	Di-n-octadecyl phosphite	1	above 140	
35		0.5	above 140	35
		0.25	above 140	
		0.1	20	
	Triphenyl phosphite	1	above 140	
		0.5	above 140	

The stabilizing efficiency of the additive is substantially increased when the additive percentage with respect to the polymer weight increases, but it is usually preferred not to increase this percentage to more than 1% by weight, in order not to impair the product mechanical properties and not to over-increase the viscosity of the composition in the molten state, since the ability to work up the composition is affected by said viscosity.

Example V.

Two compositions are prepared from 50% by weight of bis-phenol A-polycarbonate and 50% by weight of polybutylene-terephthalate. The two polymers are mixed together, in the molten state, at the temperature of 250°C. In the course of the mixing step, but 5 minutes or 10 minutes (depending on the experiment) after the two polymers are brought in contact, di-n-octadecyl phosphite is added, in the amount of 0.5% by weight.

Samples are then manufactured from the individual two compositions thus obtained, by pressing for 5 minutes, at the temperature of 240°C. The stability time, subsequently measured as at Example I, is in all cases above 140 minutes, viz. the limit of measurements.

However, in the course of the polymer mixing step preceding the incorporation of the stabilizing additive, the compositions take up a brown-yellow colour indicating the chemical reaction between polymers. Moreover, from a study of the reaction, carried out by examining the behaviour, with respect to various solvents, of compositions having reacted at a higher temperature (260°C) and for longer durations (30 and 60 minutes) and by performing infra-red spectra determinations and viscosity measurements either in the molten state or in solution, it can be assumed that said reaction induces breaking of the polymer chains, resulting in the grafting of polybutylene-terephthalate blocks onto the polycarbonate chains.

Example VI.

In the same manner as in Example III, several PC—PBT alloys are prepared using a PBT-content varying from 0 to 100% by weight, and the physical and mechanical properties of the samples are examined.

The result achieved are given in the following table. They indicate that the alloys obtained constitute a whole range of products, the properties of which vary gradually, depending on the relative percentages of the two polymers, between the properties of polycarbonate and those of polybutylene-terephthalate. However, the formation of said products is made possible by the additive, the latter ensuring the composition stabilization by preventing a noxious interaction of the two polymers.

The procedures adopted for the tests are as follows:

Crystallinity rates are determined by means of a differential micro-calorimeter (Dupont thermal analyzer) assuming the melting heat value of crystalline polybutylene-terephthalate as 34.5 cal. per gram. They are given with respect to the sample total weight.

The modulus of elasticity at 100°C and 170°C is evaluated from modulus-versus-temperature graphs plotted from measurements carried out with a Gehmann apparatus.

The impact measurements are carried out according to ASTM 1822—21T standards for the tensile impact strength, and to ISO R180 standards for the Izod impact strength.

The values of the bending modulus and the elastic limit in bending are determined according to ISO R178 standards.

PROPERTIES OF ALLOYS OF PC ($\overline{M}_w = 45,000$) and PBT ($\overline{M}_n = 41,000$)

Sample composition PC %	PBT %	Crystallinity %	Tensile impact (kg. cm/cm ²)	Izod test (kg. cm/cm)	Bending modulus (kg/cm ²)	Elastic limit (kg/cm ²)	Gehmann at 100°C (10 ⁸ dyne/cm ²)	Modulus at 170°C
100	0	0	350	150 (ductile)	19,000	1,000	240	0.3
90	10	2.2	335	—	—	—	200	0.27
80	20	6.8	310	16	22,400	1,000	160	0.35
70	30	7.8	304	—	—	—	130	0.8
60	40	10.5	275	13.5	23,000	960	110	1.8
50	50	11.8	250	10	22,500	960	90	2.7
40	60	15	230	9	22,100	960	55	4
30	70	18	163	—	—	—	42	6
20	80	20	160	8	22,000	900	34	8
10	90	23.6	154	—	—	—	34	10
0	100	27	129	6	23,000	850	34	12

Example VII.

The properties of an alloy according to the invention comprising 50% by weight of bis-phenol A-polycarbonate and 50% by weight of polybutylene-terephthalate, admixed with 0.5% by weight of di-n-octadecyl phosphite are compared with those of pure polybutylene-terephthalate. Said properties are already mentioned in the table of the previous example. Comparison shows the advantage of using the alloy according to the invention instead of polybutylene-terephthalate, in most applications thereof. It can be used, in particular, for manufacturing mechanical parts, easily obtained by injection-moulding at a temperature of about 270°C.

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The advantages of the alloy according to the invention over PBT are particularly noticeable as regards impact strength. In the case of Izod test, said resistance is improved by about 70%, and by more than 90% in the tensile impact test. The alloy exhibits a very good heat resistance, too. Its modulus at 100°C is almost three times that of pure polybutylene-terephthalate.

The increase in the impact resistance is still more marked when the samples are submitted to high temperatures for a long period of time, as shown by the following results:

	Tensile impact strength (kg.cm/cm ²)	Izod impact strength (kg.cm.cm)	
PC—PBT alloy	250	10	
after 7 days, at 100°C	191	8.6	
125°C	161	7.6	
150°C	150	7.3	
170°C	84	6.9	
Pure PBT	129	6	
after 7 days, at 170°C	11	2.1	

Thus, after, 7 days at 170°C, the alloy has still retained more than 30% of its initial impact strength, which is indicative of a resistance to thermal ageing considerably higher than that of pure polybutylene-terephthalate, the latter keeping only less than 10% of its tensile impact resistance under the same conditions.

Example VIII.

An alloy similar to that studied at example VII is prepared, except that bis-phenol A-polycarbonate (Lexan 145) having a molecular weight of 30,000 is used instead of Lexan 135 polycarbonate, which has a molecular weight of 45,000. The Izod impact strength of that alloy proved to be 9.

Example IX.

A mixture containing 50% by weight of bis-phenol A-polycarbonate and 50% of polybutylene-terephthalate, admixed with 0.5% by weight of di-n-octadecyl phosphite, is prepared according to the method disclosed for preparing PC—PBT alloys at example I. An amount of 10% by weight of glass fibres is added to the mixture, said amount being with respect to the overall weight of the thus obtained composition.

The mechanical properties of moulded samples obtained from the composition are given hereinafter and compared with those of polybutylene-terephthalate, reinforced by the same percentage of glass fibres (10% by weight of the composition):

Sample of	PBT	PC—PBT	
Tensile impact strength (kg.cm.cm ²)	40	76	
Izod impact strength (kg.cm/cm)	6.3	12.7	
Modulus of elasticity (10 ⁹ dyne/cm ²)			
at 20°C	220	220	
at 100°C	72	97	
at 175°C	35	10	

The reinforced PC—PBT alloys can undergo the same working steps and receive the same applications as reinforced polybutylene-terephthalate, but the improvement in mechanical properties clearly appears from the above results: the impact strength, expressed as the tensile impact strength as well as the Izod impact strength, is substantially twice as high, while the modulus of elasticity at 100°C is still 30% higher than that of reinforced pure PBT.

Example X.

The physical and mechanical properties of samples of PC—PBT copolymers, prepared as explained at example V, are examined. The stabilizing additive is incorporated after the reaction of the polymers has taken place for 5 or 10 minutes, respectively, at 250°C.

Crystallization speed proved to be smaller than that of the alloys in the previous example. The vitreous transition temperature, as measured from modulus of elasticity-versus-temperature graphs plotted by means of a Gehmann apparatus, is about 70°C.

Tensile impact strength is excellent and can be compared to that of pure polycarbonate; it is substantially higher than that of alloys with the same percentages of the components.

The values obtained from impact and bending tests according to the standards mentioned at example VI are given hereinafter:

Duration of reaction (minutes)	Tensile impact kg.cm/cm ²	Izod impact kg.cm/cm	Bending modulus kg/cm ²	Elastic limit kg/cm ²
5	313	8.2	22,600	920
10	320	8.1	21,100	830

Example XI.

a) In a reference experiment, a mixture of 50% polycarbonate (Lexan 135) and 50% polybutylene-terephthalate is prepared by mixing at 250°C for 5 minutes in a roller-mixer. A sample is then pressed at 270°C for 5 minutes. The thermal stability is measured at 290°C as described in example I. The result is a time of about 30 minutes;

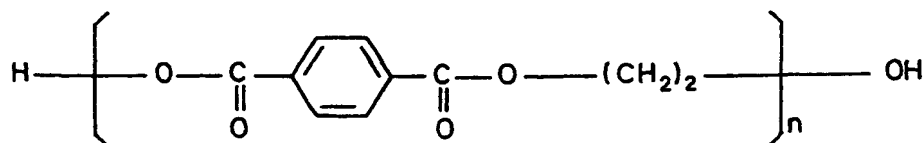
b) A mixture similar to that under (a) is prepared except that 0.5% by weight di-n-octadecyl phosphite is added to the composition. The stability time is thus raised up to 80 minutes;

c) By the same process as under (b), alloys are prepared from 50% polycarbonate and 50% polyethylene-terephthalate together with 0.5% di-n-octadecyl phosphite. The physical and chemical properties of the samples obtained from these alloys are measured. The results are shown on the following table and compared with those of pure polybutylene-terephthalate (PET).

	Pure PET	PC—PET alloy
Crystallinity (%) (+)	30.2	24.5
Tensile impact strength (kg.cm/cm ²)	62	209
Izod impact strength (kg.cm/cm)	2.4	9.8
Modulus (Gehmann) at 100°C	2.2.10 ⁹	6.9.10 ⁹
170°C	1.5.10 ⁹	2.6.10 ⁹
Bending modulus (kg/cm ²)	27,400	23,200
Elastic limit (kg/cm ²)	1,100	930

(+) calculated assuming a melting heat value of 28 cal./gr. for crystalline PET.

Polyethylene-terephthalate used in this example has the following formula:



wherein n is an integer.

Example XII

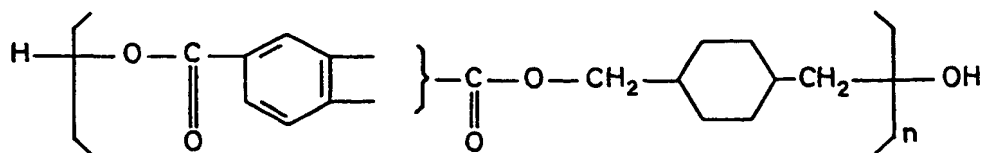
a) In a reference experiment, a mixture of 50% by weight polycarbonate (Lexan 135) and 50% polycyclohexylene dimethylene terephthalate/isophthalate is prepared by mixing at 250°C for 5 minutes in a roller-mixer. A sample is then pressed at 260°C for 5 minutes. According to the same process as in example I, the stability time is measured. The result is that this time is lower than 5 mn;

b) A mixture similar to that under (a) is prepared, except that 0.5% by weight of di-n-octadecyl-phosphite is added to the composition. In this case, the stability time is higher than 140 minutes;

c) By the same process as under (b) alloys are prepared from 50% polycarbonate, 50% polycyclo-hexylene-dimethylene terephthalate/isophthalate (PCHDT) as well as an admixture of 0.5% by weight (with respect to the weight of polymers) of di-n-octadecyl phosphite. The physical and chemical properties of the samples obtained are given with comparison to those of pure PCHDT in the following table:

	Pure PCHDT	PC—PCHDT alloy
Tensile impact strength (kg.cm/cm ²)	78	258
Izod impact strength (kg.cm/cm)	5.4	16
Bending modulus (kg/cm ²)	21,000	20,000
Elastic limit (kg/cm ²)	745	942

The polyester PCHDT used in this example has the following formula:



wherein n is an integer.

Example XIII.

The polymer components comprise 50% by weight of same PC and 50% by weight of same PBT as in example I. The composition further comprises an additive, in an amount of 0.5% by weight of the total polymer weight. The two polymers are mixed together with the additive as described in example I, the melted polymers being contacted together about 10 seconds before the additive is admixed to them.

The stability time measured as in example I is mentioned hereinafter for various acids and anhydrides used as the additives:

	<u>Additive</u>	<u>Stability time (minute)</u>	
5	None	below 5	5
	Terephthalic acid	15	
	Trimellitic acid (1,2,4-benzene-tricarboxylic acid)	12	
10	Trimesic acid (1,3,5-benzene-tricarboxylic acid)	90	10
	Pyromellitic acid (1,2,4,5-benzene-tetracarboxylic acid)	30	
15	Partially hydrolyzed anhydride of 2,3,4,5-tetrahydrofurane-tetra- carboxylic acid	30	15
	Anhydride of trimellitic acid, still comprising one acid carboxy group	26	
	Partially hydrolyzed anhydride of pyromellitic acid	25	
20	Anhydride of 1,4,5,8-naphthalene- tetracarboxylic acid	7	20

Example XIV.

25 Copolyesters are prepared as described in example V. Their crystallization rate is measured by differential microcolorimetry using a Perkin-Elmer DSC 2 apparatus. For the sample obtained after a reaction time of 5 minutes (before adding the stabilizing additive), a half crystallization time of 13 mn 10 s is measured. For the sample obtained after a reaction time of 10 minutes, no crystallization is observed with this apparatus. 25

Example XV.

30 A copolyester is prepared as described in example V, except that the PBT and the polycarbonate are contacted for 17 minutes before the additive is added. The sample is then contacted with methylene chloride for 7 hours in a Soxhlet apparatus. The solubility of the sample is about 25%. Similar values are obtained for samples maintained for a longer time at the reaction temperature (30 mn), with the additive being still added after 17 minutes. Similar values are also obtained for a reaction time of 6 minutes at 260°C, or at 270°C. 35

Example XVI.

40 Copolyesters are prepared as described in example V, using a reaction time of 10 minutes at 250°C, and varying the proportions of the components. The stability times are measured as described in Example I, as well as the impact resistance by the Izod test. The following results are obtained: 40

	Composition		Impact resistance kg.cm/cm	Stability time (MN)	
	PC % weight	PBT % weight			
5	20	80	7.5	> 100	5
	40	60	8.7	> 100	
	50	50	9.1	> 100	
	60	40	9.4	> 100	
	80	20	10.2	> 100	

Example XVII.

Following the same procedure as in example I, alloys stabilized with 0.5% by weight di-n-octadecyl phosphite are prepared from bis-phenol A-polycarbonate (Lexan 135) and a copolymer of PBT and tetramethylene-glycol. The latter is used as the commercial products from Dupont de Nemours named Hytrel 7245 (vitreous transition point of about 0°C) and Hytrel 5555 vitreous transition point of about -40°C). Mixing and moulding are carried out at 24°C.

	Composition (% by weight)	Izod impact resistance kg.cm/cm	Stability time minutes	
20	PC 70% + Hytrel (Regd. T.m.) 7245 30%	9.3	65	20
	PC 50% + Hytrel (Regd. T.m.) 7245 50%	6.9	68	
	PC 30% + Hytrel (Regd. T.m.) 7245 70%	12.9	60	
25	PC 50% + Hytrel (Regd. T.m.) 5555 50%	9.6	60	25

Example XVIII.

A mixture of PC 50% by weight, PBT 25% by weight, and PET 25% by weight is prepared according to example I and stabilized by 0.5% by weight (with respect to the total weight of the polymer mixture) of di-n-octadecylphosphite.

The Izod impact resistance of the moulded sample is 10.9 kg.cm/cm.

Example XIX.

Samples similar to those of example XV are submitted to RNM measurements to determine the copolyesterification rate, or percent conversion, by the number of terephthalic radicals carrying aromatic ester functions from the total number of carboxy groups (including all ester functions) on terephthalic radicals. The figures obtained are 9% for a reaction time of 17 minutes and 4% for a reaction time of 8 minutes, at 260°C.

Example XX.

Following the same procedure as in example V, PC—PBT copolyesters (50%—50% by weight) are prepared using 0.5% by weight trimesic acid (1,3,5-tricarboxy benzene acid) as the stabilizer, which is added to the polymer mixture after 5 or 10 minutes mixing at 250°C.

Reaction time minute	Izod impact kg.cm/cm	Stability time at 260°C (mn)
5	9.6	50
10	9.3	50

5 Quite obviously, the above examples are by no means restrictive and their variations are within the scope of the invention. 5

WHAT WE CLAIM IS:—

1. A process for preparing polyester polycarbonate compositions, as hereinbefore defined, comprising mixing at least one aromatic polyester polymer and at least one aromatic polycarbonate polymer in a reacting step wherein the polyester and the polycarbonate are contacted together in the molten state, at a temperature between 150°C and 300°C, for a time interval between 0.1 minute and 4 hours, then preventing the reaction between the polymers by adding to the melted mixture from 0.1% to 5% by weight with respect to the total polymer weight, of a stabilizing additive selected from phosphorus compounds and carboxylic acids. 10
2. A process according to Claim 1, wherein the stabilizing additive is selected from the group of organic phosphites, metaphosphonic acid, arylphosphinic, arylphosphonic acids. 15
3. A process according to Claim 1, wherein the stabilizing additive is an aromatic acid comprising a benzene, or naphthalene, or tetrahydrofuran ring carrying at least two carboxy groups. 20
4. A polymer composition comprising a polyester polymer formed between an aliphatic or cycloaliphatic diol and an aromatic diacid, a polycarbonate polymer formed between carbonic acid and an aromatic diol, and a stabilizing additive preventing the reaction between the polycarbonate and the polyester, wherein the polyester and the polycarbonate are partly copolymerized. 25
5. A polymer composition according to Claim 4, wherein from 0.1% to 80% of the total number of the carboxy groups are esterified by aromatic groups. 30
6. A polymer composition according to Claim 5, wherein said proportion number is preferably from 1% to 6%. 30

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